CANADA

DEPARTMENT OF ENERGY, MINES AND RESOURCES

MINES BRANCH

OTTAWA

PHYSICAL METALLURGY DIVISION

INTERNAL REPORT PM-M-70-8

ZIRCONIUM-REFRACTORY ALLOYS

by

H.M. Skelly and C.F. Dixon

Nuclear and Powder Metallurgy Section

March 25, 1970

PHYSICAL METALLURGY DIVISION

INTERNAL REPORT PM-M-70-8

ZIRCONIUM-REFRACTORY ALLOYS

by

H.M. Skelly* and C.F. Dixon**

- - - - -

ABSTRACT

Zirconium alloys containing thorium oxide, yttrium oxide, cerium zirconate or lanthanium oxide were prepared by arc melting. The refractories apparently dissolved in the molten zirconium and precipitated as a dispersed phase on solidification. High temperature (650°C) tensile strengths up to twice that of Zircaloy-2 were observed for arc-melted specimens.

The size and distribution of thorium oxide and cerium zirconate particles were shown to vary depending on the heat treatment, and although interparticle spacing believed to be ideal was not achieved, particles of a size considered fine enough to produce dispersion strengthening were obtained.

---

*Research Scientist and **Engineer, Nuclear and Powder Metallurgy Section, Physical Metallurgy Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

Crown Copyright Reserved.

INTRODUCTION

This investigation examines the possibility of improving the high-temperature properties of zirconium through dispersion strengthening by the addition of refractory compounds, particularly oxides, to zirconium by arc melting. To dispersion strengthen zirconium by this method it is necessary for the refractory compound to dissolve in molten zirconium, then, on cooling, to precipitate as a fine dispersion of the refractory compound itself or of some stable compound formed by its reaction with zirconium.

Because of the high reactivity of zirconium, its high solubility for oxygen, and the stability of the zirconium-oxygen solid solution, only the most stable refractories would be expected to exist in a zirconium matrix.

Thorium oxide (ThO_2), because of its high stability, was selected for initial tests. Observations were also made on the effect of additions to zirconium of yttrium oxide (Y_2O_3), lanthanum oxide (La_2O_3), and cerium zirconate ($Ce_2O_3 \cdot 2\ ZrO_2$).

The initial part of this work was previously published in a short communication [1].

EXPERIMENTAL PROCEDURE

Preparation of Alloys

The alloys listed in Table 1 were prepared using reactor-grade

zirconium sponge containing 1100 ppm oxygen. The refractory compounds were in the form of powder (3 to 4 microns in particle size).

Melting and alloying were carried out in a laboratory-size tungsten-arc furnace in an argon atmosphere. The zirconium sponge was consolidated by melting into a dense cigar-shaped ingot in which a cavity was drilled to contain the refractory compound. During melting, the refractories appeared to dissolve in the zirconium. Each charge weighed approximately 75 grams and was remelted at least 4 times to ensure homogeneity.

The Zr-0.64% Th and Zr-0.34% ZrO_2 alloys were prepared to determine the effect of thorium and oxygen in the event of any decomposition of ThO_2. The 0.64% Th and the oxygen in 0.34% ZrO_2 are approximately equivalent to the thorium and oxygen contained in 0.7% ThO_2.

The Zr-0.64% Th-0.34% ZrO_2 alloy was prepared to determine if thorium and oxygen added together would produce the same effect as 0.7% ThO_2.

The zirconium-refractory alloys are referred to by their nominal compositions.

Swaging and Heat Treating

Some arc-melted ingots were swaged in air at 500°C to 0.35-in.-diameter rod. The heat treatments listed in Tables 1 and 2 were carried out in vacuum.

Polishing and Etching

To investigate dispersed phases present in the alloys, 1/4-in. thick specimens were cut from the arc-melted ingots in the metallurgical conditions listed in Table 2. These specimens were prepared for microexamination by rough polishing on silicon carbide abrasive paper to 600 grit followed by polishing with 9-micron and 3-micron diamond paste on "Microcloth". The specimens were then chemically polished by swabbing with a solution of 45 cc nitric acid and 9 to 10 cc hydrofluoric acid in 45 cc distilled water.

For examination by the electron microscope, specimens were polished as above and replicas of the structures were taken using a 2% formvar solution.

X-Ray Diffraction Analysis

X-ray diffraction analysis of Zr-2.5% ThO_2, Zr-3% $Ce_2O_3 . 2ZrO_2$, and Zr-2% Y_2O_3 alloys were carried out on a GE diffractometer using CuK alpha radiation. The specimens were prepared for X-ray analysis in the same manner as described under "Polishing and Etching".

X-ray diffraction analysis and X-ray fluorescence analysis were also carried out on particles chemically extracted from the Zr-3% $Ce_2O_3 . 2ZrO_2$ alloy by selective solution treatment with bromine methanol.

Tensile Testing

Tensile tests were carried out on specimens in the metallurgical conditions listed in Table 1. Specimens were tested at 650°C in a vacuum of 5×10^{-5} mm mercury using an Instron universal testing machine.

The test specimens were of 1-in. gauge length and 0.16-in. gauge diameter. Each specimen was held at temperature for 1 hr before testing and all tests were in duplicate.

Oxygen Analysis

Specimens of arc-melted alloys containing 0.7% ThO_2, 0.64% Th, 0.34% ZrO_2, and 0.64% Th plus 0.34% ZrO_2 were analysed for oxygen by the vacuum fusion method.

RESULTS

Examination of Microstructure

Results of microexamination of experimental alloys listed in Table 2 are shown in the photomicrographs (Figures 1, 2, 8, and 9) and in the electron micrographs (Figures 3 to 7 and 10).

Microstructures of the Zr-0.64% Th and Zr-0.7% ThO_2 alloys, after swaging at 500°C followed by heat treating at 700°C for 6 hr, are shown in Figures 1 and 2 respectively. A dispersed second phase is evident in the Zr-0.7% ThO_2 alloy (Figure 2) but no second-phase particles are evident at this magnification (X150) in the Zr-0.64% Th alloy (Figure 1). There were insufficient second-phase particles present in Zr-0.7% ThO_2 to permit identification by X-ray diffraction analysis but a dispersed phase present in an arc-melted Zr-2.5% ThO_2 alloy (Figure 3) was identified by X-ray diffraction analysis as ThO_2.

Figures 3 to 7 show the effect of heat treatment on the size, distribution and solubility of ThO_2 in the Zr-2.5% ThO_2 alloy. Figure 3 shows ThO_2 at the alpha platelet boundaries. Heat treating at 800°C for 24 hr and water quenching caused the ThO_2 to coalesce (Figure 4). X-ray diffraction analysis of this specimen confirmed that the particles were ThO_2. In the microstructure of specimens heat treated at 950°C and shown in Figure 5, the ThO_2 is at the boundaries of alpha platelets which are much finer than those in the arc-melted specimens. Thin specimens quenched from this temperature (950°C) into brine at 6°C produced a structure in which ThO_2 particles were distributed throughout the matrix as shown in Figure 6. The ThO_2 particles in specimens heat treated in a vacuum furnace at 1400°C for 24 hr and furnace cooled were as large as 3 microns (Figure 7).

Microexamination of specimens containing 0.64% Th plus 0.34% ZrO_2 did not reveal any evidence of dispersed particles.

The microstructure of arc-melted Zr-3% $Ce_2O_3 \cdot 2ZrO_2$ alloy is shown in Figure 8. The particles at the alpha platelet boundaries were chemically extracted and identified as $Ce_2O_3 \cdot 2ZrO_2$ by X-ray analysis. After a specimen of this alloy had been heated at 950°C for 6 hr when water quenched, the particles were much finer ($\sim$ 0.1 μ) and were distributed as

shown in Figures 9 and 10.

The Zr-2% Y_2O_3 alloy contained particles at former beta grain boundaries and throughout the matrix. These particles were identified as Y_2O_3 by X-ray diffraction.

Tensile Tests

Table 1 lists the results of the tensile tests. Values for zirconium and Zircaloy-2 are included for comparison.

All the alloys containing 2.5% or more ThO_2 had high-temperature (650°C) tensile strengths greater than Zircaloy-2. No significant effect on the strength was observed after the ThO_2 content had been increased from 3.5% to 7%, or after Zr-2.5% ThO_2 specimens had been heat treated at 650°C or 950°C for 6 hr. However, after specimens of the Zr-0.7% ThO_2 alloy had been swaged at 500°C and heat treated at 700°C for 6 hr, the ultimate tensile strength increased to 23.6 kpsi from 16.2 kpsi for arc-melted specimens.

It can be seen that the tensile strengths of Zr-0.64% Th, Zr-0.34% ZrO_2 and Zr-0.64% Th-0.34% ZrO_2 were less than half that of Zr-0.7% ThO_2 swaged and heat treated, and substantially below that of Zr-0.7% ThO_2 as arc-melted.

The addition of $Ce_2O_3 . 2ZrO_2$, Y_2O_3, and La_2O_3 also produced strengthening. The strength of the Zr-$Ce_2O_3 . 2ZrO_2$ alloys increased progressively with refractory content. The alloy containing 7% $Ce_2O_3 . 2ZrO_2$

had an ultimate strength of 36 kpsi. Hot swaging the Zr-1% $Ce_2O_3 . 2ZrO_2$ alloy also increased the tensile strength. Alloys containing Y_2O_3 showed a maximum ultimate tensile strength of 24 kpsi at 3% Y_2O_3. Addition of 0.5% La_2O_3 produced as much strengthening as additions of 1% and 2% La_2O_3.

Oxygen Analysis

The oxygen analysis results given in Table 3 show that addition of 0.34% ZrO_2 to zirconium and to Zr-0.64% Th was effective in increasing the oxygen content to the same level as that in Zr-0.7% ThO_2 alloy.

DISCUSSION

Dispersed Phase

Microexamination and X-ray analysis of arc-melted zirconium-refractory alloys show that ThO_2, $Ce_2O_3 . 2ZrO_2$ and Y_2O_3 are present as discrete particles.

Comparison of Figures 3 (Zr-2.5% ThO_2, arc-melted) and 4 (Zr-2.5 ThO_2, H.T. 800°C 6 hr, water quenched)indicates that some coalescence of ThO_2 particles has occurred on heat treating at 800°C. Redistribution of ThO_2 on alpha platelet boundaries after Zr-2.5% ThO_2 specimens were water quenched from 950°C (compare Figures 3 and 5) suggests that the ThO_2 was soluble in zirconium at this temperature and precipitated on cooling. As shown in Figure 6, faster cooling of specimens by quenching thin sections into brine at 6°C caused the ThO_2 to precipitate as a dispersed phase in the matrix. Furnace cooling of specimens from 1400°C

allowed time for ThO_2 particles to grow in size (Figure 7).

From the above, it would appear that ThO_2 is sufficiently soluble in zirconium at 800°C to coalesce and that 2.5% ThO_2 is completely soluble at 950°C.

The change in size and distribution of the refractory when the Zr-3% $Ce_2O_3 \cdot 2ZrO_2$ alloy was water quenched from 950°C suggests that 3% $Ce_2O_3 \cdot 2ZrO_2$ is almost completely dissolved in zirconium at this temperature (compare Figures 8 and 9).

Tensile Properties

The Zr-0.7% ThO_2 alloy had a high-temperature strength superior to that of the Zr-0.64% Th alloy, the Zr-0.34% ZrO_2 alloy, and the Zr-0.64% Th-0.34% ZrO_2 alloy (Table 1). The presence of added oxygen would not be expected to influence the tensile strength of these alloys according to Weinstein and Holtz [2] and Miller [3], and the results confirm this. The strength superiority of this alloy, therefore, is not due to solution in zirconium of thorium or oxygen but must be due to the presence of the ThO_2 particles. It is, therefore, reasonable to conclude that the increase in strength of the other Zr-ThO_2 alloys is likewise due to the presence of the refractory particles.

The results in Table 1 show that $Ce_2O_3 \cdot 2ZrO_2$, Y_2O_3 and La_2O_3 additions also improve the tensile strength of zirconium at 650°C.

Values given in the literature for the particle size and interparticle spacing that produce dispersion strengthening in Ni-ThO_2 and Al-Al_2O_3 systems range from less than 0.1 to 0.25 micron for the particles and

from 0.1 to 1.0 micron for the spacing [4-9]. Microexamination of the arc-melted Zr-2.5% ThO_2 and Zr-3% $Ce_2O_3 \cdot 2ZrO_2$ alloys (Figures 3 and 8) showed that the dispersed phases did not match these dimensions. Dispersed particles about 0.1-micron diameter were obtained by heat treating these alloys at 950°C for 6 hr and quenching (Figures 6 and 10), but the interparticle spacing remained too large.

CONCLUSIONS

Arc melting zirconium with additions of ThO_2, Y_2O_3, or $Ce_2O_3 \cdot 2ZrO_2$ results in a dispersion of the refractory compound in the alloy.

Alloys with high-temperature (650°C) tensile strengths up to twice that of Zircaloy-2 can be produced by arc melting zirconium with additions of refractory compounds.

The high-temperature strength of Zr-ThO_2 alloys is not due to solution in zirconium of thorium or oxygen arising from any decomposition of ThO_2.

The size and distribution of the ThO_2 and $Ce_2O_3 \cdot 2ZrO_2$ particles in zirconium can be varied by heat treatment. However, the interparticle spacing necessary for dispersion strengthening was not achieved in this work.

ACKNOWLEDGEMENTS

The authors wish to thank Miss J. Ng-Yelim for assistance in obtaining the electron micrographs, Dr. C.M. Mitchell for X-ray diffraction analysis, and Mr. L. Ripley of the Mineral Science Division for his assistance in isolating and identifying the $Ce_2O_3 \cdot 2ZrO_2$ dispersion.

REFERENCES

1. C.F. Dixon and H.M. Skelly, "Addition of Refractory Compounds to Molten Zirconium" - J. Less - Common Metals, 18 (1969) 440.
2. D. Weinstein and F.C. Holtz, "On Dispersion Strengthening of Zirconium" - Trans. AIME, 227 (1963) 1463.
3. G.L. Miller, "Zirconium" - Butterworth's Scientific Publications, 2nd ed., London, 1957, p. 253.
4. Fred J. Anders, Jr., Guy B. Alexander and William S. Wartel, "A Dispersion-Strengthened Nickel Alloy" - Metal Progress, Dec. (1962), 88.
5. Niels Hansen, "Dispersion-Strengthened Aluminum Products" - Danish Atomic Energy Commission, Research Establishment Risö, Risö Report No. 113 (May 1966).

6. R.W. Fraser, B. Meddings, D.J.I. Evans and V.N. Mackiw, "Dispersion-Strengthened Nickel by Compaction and Rolling of Powder by Pressure Hydrometallurgy" - Modern Developments in Powder Metallurgy, Ed. Henry H. Hausner, Vol. 2 Applications, Plenum Press, New York, 1966, p. 87.

7. P. Guyot, "On the Mechanisms of Plastic Deformation of SAP-Type Alloys" - ibid, p. 112.

8. S.M. Wolf, "Properties and Applications of Dispersion-Strengthened Metals" - J. of Metals 19 (1967), 22.

9. D.W. Ashall and P.E. Evans, "Yielding and Work-Hardening in Ni-ThO_2 Alloys" - Metal Science J., 2 (1968), 96.

HMS:CFD:lm

TABLE 1

Tensile Properties of Zirconium and Zirconium Alloys at 650°C

Nominal Composition	Condition	UTS, kpsi	.2% YS, kpsi	% El on 1 in.
Zr	As Arc-Melted	11.2	7.5	44
Zircaloy-2	As Arc-Melted	17.6	11.9	42
Zr-0.64% Th	Swaged 500°C, HT 700°C 6 hr, WQ	9.5	4.7	63
Zr-0.34% ZrO_2	Swaged 500°C, HT 700°C 6 hr, WQ	10.0	5.6	59
Zr-0.64% Th-0.34% ZrO_2	Swaged 500°C, HT 700°C 6 hr, WQ	9.7	4.0	66
Zr-0.7% ThO_2	Swaged 500°C, HT 700°C 6 hr, WQ	23.6	14.7	48
Zr-0.7% ThO_2	As Arc-Melted	16.2	10.9	36
Zr-2.5% ThO_2	As Arc-Melted	23.7	16.8	27
Zr-3.5% ThO_2	As Arc-Melted	27.0	17.3	35
Zr-5.0% ThO_2	As Arc-Melted	26.6	17.7	26
Zr-7.0% ThO_2	As Arc-Melted	25.5	16.3	20
Zr-2.5% ThO_2	HT 650°C 6 hr, WQ	26.1	17.5	22
Zr-2.5% ThO_2	HT 950°C 6 hr, WQ	23.7	16.5	27
Zr-1% $Ce_2O_3 . 2ZrO_2$	Swaged 500°C	19.9	11.9	36
Zr-1% $Ce_2O_3 . 2ZrO_2$	As Arc-Melted	15.2	9.3	36
Zr-3% $Ce_2O_3 . 2ZrO_2$	As Arc-Melted	20.6	13.6	8
Zr-5% $Ce_2O_3 . 2ZrO_2$	As Arc-Melted	27.4	18.3	8
Zr-7% $Ce_2O_3 . 2ZrO_2$	As Arc-Melted	36.0	25.7	14
Zr-1% Y_2O_3	As Arc-Melted	19.5	13.2	20
Zr-2% Y_2O_3	As Arc-Melted	21.6	14.6	26
Zr-3% Y_2O_3	As Arc-Melted	24.0	15.3	24
Zr-5% Y_2O_3	As Arc-Melted	19.2	12.3	22
Zr-0.5% La_2O_3	As Arc-Melted	19.3	12.0	28
Zr-1% La_2O_3	As Arc-Melted	19.8	12.5	32
Zr-2% La_2O_3	As Arc-Melted	17.1	10.9	27

W.Q. - Water Quenched.
H.T. - Heat Treated.

TABLE 2

Zr-Th and Zr-Refractory Alloys used for Observation of Dispersed Phase

Nominal Composition	Condition
Zr-0.64% Th	Swaged 500°C, H.T. 700°C 6 hr, W.Q.
Zr-0.7% ThO_2	Swaged 500°C, H.T. 700°C 6 hr, W.Q.
Zr-0.64% Th-0.34% ZrO_2	Swaged 500°C, H.T. 700°C 6 hr, W.Q.
Zr-2.5% ThO_2	Arc-Melted
Zr-2.5% ThO_2	H.T. 800°C 24 hr, W.Q.
Zr-2.5% ThO_2	H.T. 950°C 6 hr, W.Q.
Zr-2.5% ThO_2	H.T. 950°C 6 hr, Quenched in Brine at 6°C.
Zr-2.5% ThO_2	H.T. 1400°C 24 hr, Furnace Cooled.
Zr-3% Ce_2O_3 .2 ZrO_2	Arc-Melted
Zr-3% Ce_2O_3 .2 ZrO_2	H.T. 950°C 6 hr, W.Q.
Zr-2% Y_2O_3	Arc-Melted
Zr-2% Y_2O_3	H.T. 850°C 6 hr, W.Q.

W.Q. - Water Quenched.
H.T. - Heat Treated.

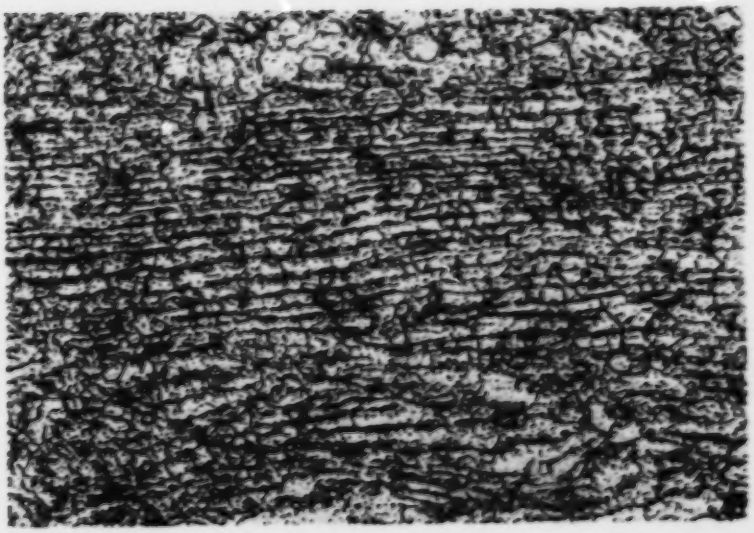
TABLE 3

Oxygen Content of Samples Swaged at 500°C Then Heat Treated at 700°C for 6 Hours

Nominal Composition	Oxygen Content (wt %)
Zr-0.7% ThO_2	0.20
Zr-0.64% Th	0.11
Zr-0.34% ZrO_2	0.20
Zr-0.64% Th - 0.34% ZrO_2	0.20

X150

Figure 1. Zr-0.64% Th.
Swaged 500°C, H.T. 700°C 6 hr, W.Q.



X150

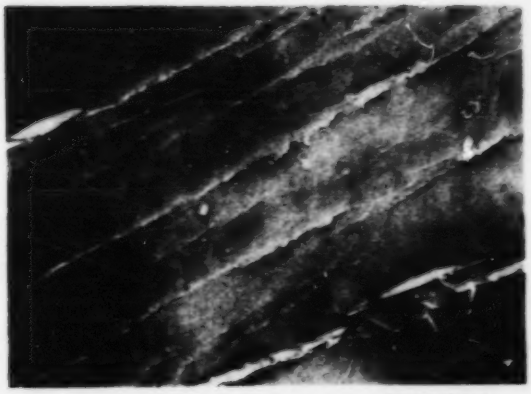
Figure 2. Zr-0.7% ThO_2.
Swaged 500°C, H.T. 700°C 6 hr, W.Q.

X5,000

Figure 3. Zr-2.5% ThO_2.
Arc-Melted.

X5,000

Figure 4. Zr-2.5% ThO_2.
HT 800°C 6 hr, W.Q.

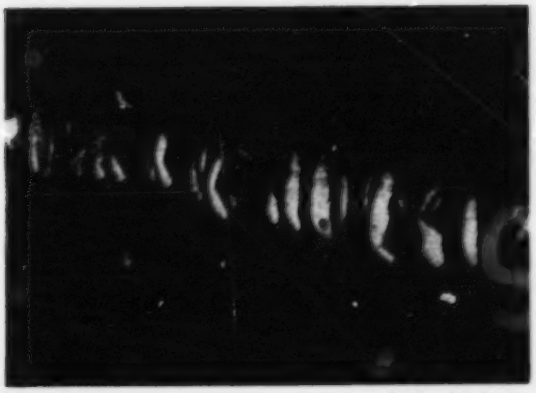


X5,000

Figure 5. Zr-2.5% ThO_2.
HT 950°C 6 hr, WQ.

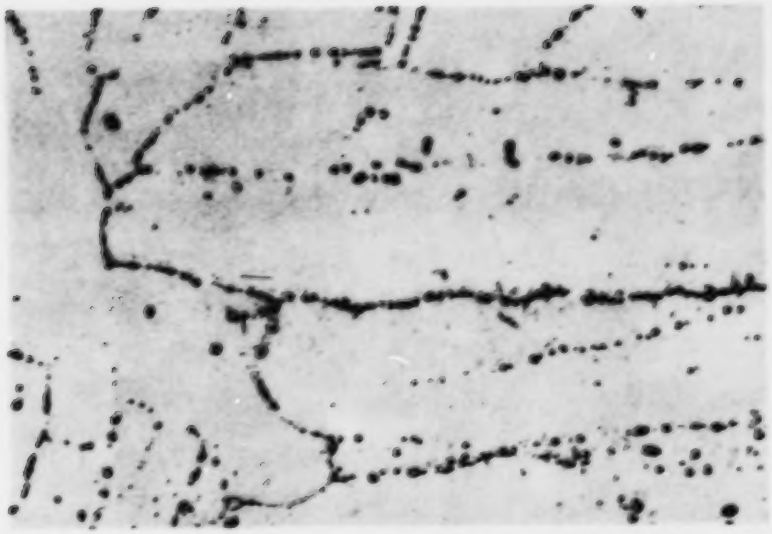
X5,000

Figure 6. Zr-2.5% ThO_2.
HT 950°C 6 hr.
Quenched into Brine at 6°C.



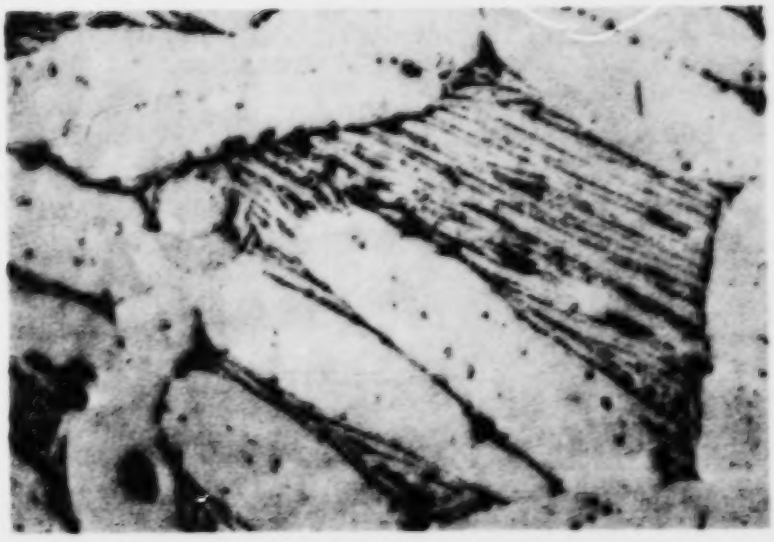
X5,000

Figure 7. Zr-2.5% ThO_2.
HT 1400°C 24 hr.
Furnace Cooled.



X1,000

Figure 8. Zr-3% Ce_2O_3 .$2ZrO_2$.
Arc-Melted.



X1,000

Figure 9. Zr-3% Ce_2O_3 .$2ZrO_2$.
HT 950°C 6 hr, WQ.

X8,500

Figure 10. Zr-3% Ce_2O_3 .$2ZrO_2$.
HT 950°C 6 hr, WQ.

Figure 1. Zr-0.64% Th. Swaged 500°C, H.T. 700°C 6 hr, W.Q.

Figure 2. Zr-0.7% ThO_2. Swaged 500°C, H.T. 700°C 6 hr, W.Q.

Figure 3. Zr-2.5% ThO_2. Arc-Melted.

Figure 4. Zr-2.5% ThO_2. HT 800°C 6 hr, W.Q.

Figure 5. Zr-2.5% ThO_2. HT 950°C 6 hr, WQ.

Figure 6. Zr-2.5% ThO_2. HT 950°C 6 hr. Quenched into Brine at 6°C.

Figure 7. Zr-2.5% ThO_2. HT 1400°C 24 hr. Furnace Cooled.

Figure 8. Zr-3% Ce_2O_3 .$2ZrO_2$. Arc-Melted.

Figure 9. Zr-3% Ce_2O_3 .$2ZrO_2$. HT 950°C 6 hr, WQ.

Figure 10. Zr-3% Ce_2O_3 .$2ZrO_2$. HT 950°C 6 hr, WQ.